

TITLE

**PERFLUOROELASTOMER ARTICLES HAVING IMPROVED SURFACE
PROPERTIES**

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CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims the benefit of U.S. Provisional Application No. 60/414,230 filed September 27, 2002.

FIELD OF THE INVENTION

10 This invention relates to perfluoroelastomer articles having improved surface lubricity. More specifically, this invention relates to perfluoroelastomer articles coated with a thin film of a composition comprising a polysiloxane and a urethane oligomer.

BACKGROUND OF THE INVENTION

15 Perfluoroelastomers have achieved outstanding commercial success and are used in a wide variety of applications in which severe environments are encountered, in particular those end uses where exposure to high temperatures and aggressive chemicals occurs. For example, these polymers are often used in seals for aircraft engines, in oil-
20 well drilling devices, and in sealing elements for industrial equipment used at high temperatures.

The outstanding properties of perfluoroelastomers are largely attributable to the stability and inertness of the copolymerized perfluorinated monomer units that make up the major portion of the
25 polymer backbones in these compositions. Such monomers include tetrafluoroethylene and perfluorinated vinyl ethers. In order to develop elastomeric properties fully, perfluoroelastomers are typically crosslinked, i.e. vulcanized. To this end, a small amount of cure site monomer is copolymerized with the perfluorinated monomer units. Cure site
30 monomers containing at least one nitrile group, for example perfluoro-8-

cyno-5-methyl-3,6-dioxa-1-octene, are especially preferred. Such compositions are described in U.S. Patents 4,281,092; 4,394,489; 5,789,489; and 5,789,509.

In certain end use applications, a cured perfluoroelastomer article

5 may undesirably adhere to the surface of other materials that are in contact with it, particularly if the perfluoroelastomer article and other material are forcibly held in contact for a long period of time at elevated pressures and temperatures, and then cooled. It may be difficult, or impossible, to easily remove the perfluoroelastomer article from contact

10 with the other material without damaging the perfluoroelastomer article, other material, or both. Also, the perfluoroelastomer article may be undesirably pulled from the groove in which it is seated when the article is being separated from a surface to which it has adhered. Thus, there is a need for perfluoroelastomer articles that have an improved, less sticky

15 surface.

Kishino et al. (U.S. Patent No. 5,763,068) disclose fluororesin-coated fluoroelastomer articles. In contrast to perfluoroelastomers, fluoroelastomers contain copolymerized units of at least one monomer which is either partially fluorinated (such as vinylidene fluoride), or non-20 fluorinated (such as propylene). The articles are made by first blending uncured fluoroelastomer with up to 50 parts fluororesin; shaping the blend into an article and curing it; coating the cured article with an aqueous fluororesin dispersion; drying the coated article; and finally heating the article above the melting point of the fluororesin in order to form a durable

25 fluororesin film coating. However, blending a high level of fluororesin with a fluoroelastomer or perfluoroelastomer typically reduces the physical properties of cured articles produced from such blends, especially if the articles are used in a high temperature environment. Compression set resistance and elongation are particularly adversely effected. Heating

30 fluoroelastomer articles to a temperature of about 300°C or higher, in

order to melt the fluororesin, may further degrade the physical properties of the articles.

Tarney et al. (WO 02/20650) disclose fluoropolymer coated perfluoroelastomer articles which have good physical properties and a low 5 stick surface. However, in demanding applications which require excellent high vacuum sealing performance, Tarney's articles may leak due to the nature of the surface coating. Thus, there is a need for perfluoroelastomer articles that have an improved, less sticky surface and which have excellent sealing performance in high vacuum applications such as in 10 some semiconductor manufacturing equipment.

SUMMARY OF THE INVENTION

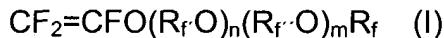
An aspect of this invention is a cured perfluoroelastomer article having a surface coated with a film comprising a polysiloxane and a urethane oligomer.

15 Another aspect of this invention is a process comprising:

- A. coating a cured perfluoroelastomer article with a dispersion comprising i) a polysiloxane having pendant hydroxyl groups and ii) a blocked isocyanate to form a wet-coated perfluoroelastomer article;
- 20 B. drying said wet-coated perfluoroelastomer article to form a dry-coated perfluoroelastomer article at a temperature below which said pendant hydroxyl groups react with said blocked isocyanate to form urethane oligomer; and
- C. heating said dry-coated perfluoroelastomer article to a 25 temperature and for a sufficient period of time where said pendant hydroxyl groups react with said blocked isocyanate to form urethane oligomer and a durable film comprising said polysiloxane and urethane oligomer on the surface of said perfluoroelastomer article.

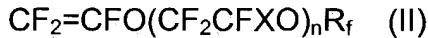
DETAILED DESCRIPTION OF THE INVENTION

Perfluoroelastomers are polymeric compositions having copolymerized units of at least two principal perfluorinated monomers. Generally, one of the principal comonomers is a perfluoroolefin while the 5 other is a perfluorovinyl ether. Representative perfluorinated olefins include tetrafluoroethylene and hexafluoropropylene. Suitable perfluorinated vinyl ethers include those of the formula



where R_f and R_f are different linear or branched perfluoroalkylene groups of 2-6 carbon atoms, m and n are independently 0-10, and R_f is a perfluoroalkyl group of 1-6 carbon atoms.

A preferred class of perfluorinated vinyl ethers includes compositions of the formula



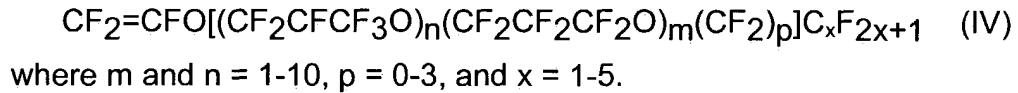
15 where X is F or CF_3 , n is 0-5, and R_f is a perfluoroalkyl group of 1-6 carbon atoms.

Most preferred perfluorinated vinyl ethers are those wherein n is 0 or 1 and R_f contains 1-3 carbon atoms. Examples of such perfluorinated ethers include perfluoro(methyl vinyl) ether and perfluoro(propyl vinyl) ether. Other useful monomers include compounds of the formula



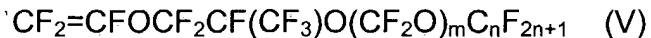
where R_f is a perfluoroalkyl group having 1-6 carbon atoms, m = 0 or 1, n = 0-5, and Z = F or CF_3 .

Preferred members of this class are those in which R_f is C_3F_7 , m = 0, and 25 n = 1. Additional perfluorinated vinyl ether monomers include compounds of the formula



Preferred members of this class include compounds where n = 0-1, m = 0-1, and x = 1.

Additional examples of useful perfluorinated vinyl ethers include



where $n = 1-5$, $m = 1-3$, and where, preferably, $n = 1$.

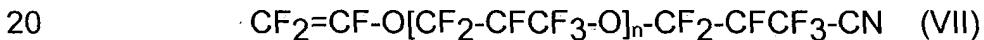
Preferred perfluoroelastomer copolymers are comprised of

5 tetrafluoroethylene and at least one perfluorinated vinyl ether as principal monomer units. In such copolymers, the copolymerized perfluorinated ether units constitute from about 15-50 mole percent of total monomer units in the polymer.

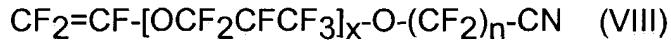
The perfluoroelastomer further contains copolymerized units of at 10 least one cure site monomer, generally in amounts of from 0.1-5 mole percent. The range is preferably between 0.3-1.5 mole percent. Although more than one type of cure site monomer may be present, most commonly one cure site monomer is used and it contains at least one nitrile substituent group. Suitable cure site monomers include nitrile-containing 15 fluorinated olefins and nitrile-containing fluorinated vinyl ethers. Useful nitrile-containing cure site monomers include those of the formulas shown below.



where $n = 2-12$, preferably 2-6;

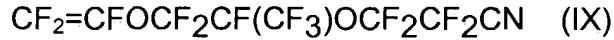


where $n = 0-4$, preferably 0-2; and



where $x = 1-2$, and $n = 1-4$.

Those of formula (VIII) are preferred. Especially preferred cure site 25 monomers are perfluorinated polyethers having a nitrile group and a trifluorovinyl ether group. A most preferred cure site monomer is



i.e. perfluoro(8-cyano-5-methyl-3,6-dioxa-1-octene) or 8-CNVE.

Other cure site monomers include olefins represented by the 30 formula $\text{R}_1\text{CH=CR}_2\text{R}_3$, wherein R_1 and R_2 are independently selected from hydrogen and fluorine and R_3 is independently selected from hydrogen,

fluorine, alkyl, and perfluoroalkyl. The perfluoroalkyl group may contain up to about 12 carbon atoms. However, perfluoroalkyl groups of up to 4 carbon atoms are preferred. In addition, the cure site monomer preferably has no more than three hydrogen atoms. Examples of such olefins

5 include ethylene, vinylidene fluoride, vinyl fluoride, trifluoroethylene, 1-hydropentafluoropropene, and 2-hydropentafluoropropene, as well as brominated olefins such as 4-bromo-3,3,4,4-tetrafluorobutene-1 and bromotrifluoroethylene. Alternatively, or in addition to copolymerized units of cure site monomers, cure sites of bromine or iodine-containing end

10 groups may be introduced onto the perfluoroelastomer polymer chain by the reaction of bromine or iodine-containing chain transfer agents during polymerization.

Another type of cure site monomer which may be incorporated in the perfluoroelastomers employed in this invention is perfluoro(2-phenoxypropyl vinyl ether) and related monomers as disclosed in U.S. Patent No. 3,467,638.

An especially preferred perfluoroelastomer contains 53.0-79.9 mole percent tetrafluoroethylene, 20.0-46.9 mole percent perfluoro(methyl vinyl) ether and 0.4 to 1.5 mole percent nitrile-containing cure site monomer.

20 When the perfluoroelastomer has copolymerized units of a nitrile-containing cure site monomer, a cure system based on an organotin compound can be utilized. Suitable organotin compounds include allyl-, propargyl-, triphenyl- and allenyl tin curatives. Tetraalkyltin compounds or tetraaryltin compounds are the preferred curing agents for use in

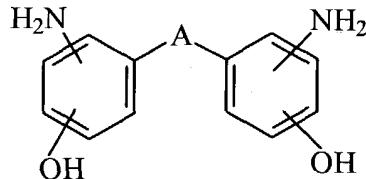
25 conjunction with nitrile-substituted cure sites. The amount of curing agent employed will necessarily depend on the degree of crosslinking desired in the final product as well as the type and concentration of reactive moieties in the perfluoroelastomer. In general, about 0.5-10 parts by weight per 100 parts elastomer (phr) of curing agent can be used, and 1-4 phr is

30 satisfactory for most purposes. It is believed that the nitrile groups trimerize to form s-triazine rings in the presence of curing agents such as

organotin, thereby crosslinking the perfluoroelastomer. The crosslinks are thermally stable, even at temperatures of 275°C and above.

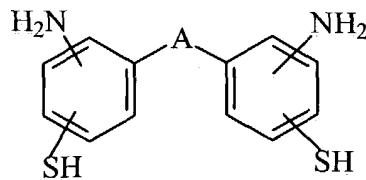
A preferred cure system, useful for perfluoroelastomers containing nitrile-containing cure sites, utilizes bis(aminophenols) and

5 bis(aminothiophenols) of the formulas



(XII)

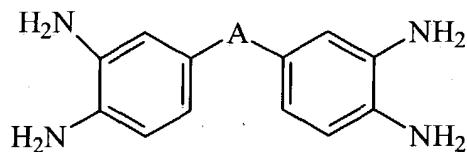
and



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(XIII)

and tetraamines of the formula



(XIV)

15 where A is SO₂, O, CO, alkyl of 1-6 carbon atoms, perfluoroalkyl of 1-10 carbon atoms, or a carbon-carbon bond linking the two aromatic rings.

The amino and hydroxyl or thio groups in formulas XII and XIII above are adjacent to each other on the benzene rings and are interchangeably in the meta and para positions with respect to the group A. Preferably, the

20 curing agent is a compound selected from the group consisting of 4,4'-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]bis(2-aminophenol); 4,4'-sulfonylbis(2-aminophenol); 3,3'-diaminobenzidine; and 3,3',4,4'-

tetraaminobenzophenone. The first of these is the most preferred and will be referred to as bis(aminophenol) AF. The curing agents can be prepared as disclosed in U.S. Patent Number 3,332,907 to Angelo.

5 Bis(aminophenol) AF can be prepared by nitration of 4,4'-[2,2,2-trifluoro-1- (trifluoromethyl)ethylidene]-bisphenol (i.e. bisphenol AF), preferably with potassium nitrate and trifluoroacetic acid, followed by catalytic hydrogenation, preferably with ethanol as a solvent and a catalytic amount of palladium on carbon as catalyst. The level of curing agent should be chosen to optimize the desired properties of the vulcanizate. In general, a

10 slight excess of curing agent over the amount required to react with all the cure sites present in the perfluoroelastomer is used. Typically, 0.5-5.0 parts by weight of the curative per 100 parts of elastomer is required. The preferred range is 1.0-2.0 phr.

Peroxides may also be utilized as curing agents, particularly when

15 the cures site is a nitrile group or an iodine or bromine group. Useful peroxides are those which generate free radicals at curing temperatures. A dialkyl peroxide or a bis(dialkyl peroxide) which decomposes at a temperature above 50°C is especially preferred. In many cases it is preferred to use a ditertiarybutyl peroxide having a tertiary carbon atom

20 attached to peroxy oxygen. Among the most useful peroxides of this type are 2,5-dimethyl-2,5-di(tertiarybutylperoxy)hexyne-3 and 2,5-dimethyl-2,5-di(tertiarybutylperoxy)hexane. Other peroxides can be selected from such compounds as dicumyl peroxide, dibenzoyl peroxide, tertiarybutyl perbenzoate, and di[1,3-dimethyl-3-(t-butylperoxy)butyl]carbonate.

25 Generally, about 1-3 parts of peroxide per 100 parts of perfluoroelastomer is used. Another material which is usually blended with the composition as a part of the peroxide curative system is a coagent composed of a polyunsaturated compound which is capable of cooperating with the peroxide to provide a useful cure. These coagents can be added in an

30 amount between 0.1 and 10 parts per 100 parts perfluoroelastomer, preferably between 2-5 phr. The coagent may be one or more of the

following compounds: triallyl cyanurate; triallyl isocyanurate; tri(methylallyl)isocyanurate; tris(diallylamine)-s-triazine; triallyl phosphite; N,N-diallyl acrylamide; hexaallyl phosphoramide; N,N,N',N'-tetraalkyl tetraphthalamide; N,N,N',N'-tetraallyl malonamide; trivinyl isocyanurate;

5 2,4,6-trivinyl methyltrisiloxane; and tri(5-norbornene-2-methylene)cyanurate. Particularly useful is triallyl isocyanurate.

Other curatives suitable for vulcanizing perfluoroelastomers having nitrile cure sites include ammonia, the ammonium salts of inorganic or organic acids (e.g. ammonium perfluorooctanoate) as disclosed in U.S. 10 Patent No. 5,565,512, and compounds (e.g. urea) which decompose to produce ammonia as disclosed in U.S. Patent No. 6,281,296 B1.

Depending on the cure site monomers present, it is also possible to use a dual cure system. For example, perfluoroelastomers having copolymerized units of nitrile-containing cure site monomers can be cured 15 using a curative comprising a mixture of a peroxide in combination with an organotin curative and a coagent. Generally, 0.3-5 parts of peroxide, 0.3-5 parts of coagent, and 0.1-10 parts of organotin curative are utilized.

Additives, such as fillers (e.g. non-fibrillating and fibrillating fluoropolymers, carbon black, barium sulfate, silica, aluminum oxide, 20 aluminum silicate, and titanium dioxide), stabilizers, plasticizers, lubricants, and processing aids typically utilized in perfluoroelastomer compounding can be incorporated into the compositions of the present invention, provided they have adequate stability for the intended service conditions.

25 Cured perfluoroelastomer articles employed in this invention are made by shaping and then curing the above perfluoroelastomer compositions. Curing may be induced by heat or by radiation. The article may subsequently be post cured at elevated temperatures for a period of time.

30 After extensive research, a polymeric coating composition has been found which provides perfluoroelastomer articles having both low surface

stickiness and good sealing properties. The durable films which coat the perfluoroelastomer articles employed in this invention are comprised of at least one polysiloxane and at least one urethane oligomer. Pendant functional groups on the polysiloxane (e.g. hydroxyl groups) react during 5 film curing with a compound in the coating mixture having pendant isocyanate groups to form covalent bonds (i.e. a urethane oligomer).

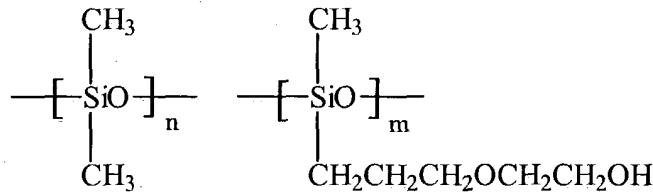
Mixtures of polysiloxanes that contain functional groups capable of reacting with isocyanate groups and non-reactive polysiloxanes may be employed in the coating compositions of this invention.

10 Examples of isocyanates that may be employed in this invention include, but are not limited to diphenylmethane diisocyanate, hexamethylene diisocyanate, tolylene diisocyanate, xylylene diisocyanate, and 4,4'-methylene bis(cyclohexyl isocyanate).

15 Prior to curing the coating composition onto the perfluoroelastomer part, the isocyanate is in the form of a derivative (i.e. a blocked isocyanate) which is unreactive with the pendant functional groups on the polysiloxane. Such derivatives are formed by reacting one or more compounds such as phenols, oximes, mercaptans, acid amides, acid imides, imidazoles, ureas, amines, or imides with the isocyanate. At 20 elevated temperature (e.g. the film curing temperature), the derivatives dissociate, leaving the isocyanate groups to react with pendant functional groups on the polysiloxane, forming the urethane oligomer.

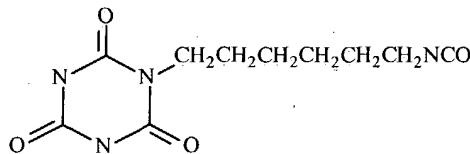
A preferred uncured coating composition for use in this invention comprises i) a mixture of the polysiloxanes

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wherein the values of n and m are such that the number average molecular weights of the two polysiloxanes are between 500 and 5000 (as

measured by size exclusion chromatography employing polystyrene calibration standards), and ii) the isocyanate



blocked with 2-butanone oxime.

5

Preferably the ratio of polysiloxanes to isocyanate is approximately 7:3 (by weight). Such a mixture is commercially available as SAT No. 7 from Shinko Technical Research Company, Ltd., Tokyo, Japan.

In the process of this invention, the uncured polysiloxane - blocked 10 isocyanate coating composition is applied as a dispersion to a cured perfluoroelastomer article. Liquids other than water (e.g. ethyl acetate) may be used to form the dispersion. The dispersion typically comprises between 5 and 10 weight percent polysiloxane, based on the total weight of the dispersion. The weight ratio of polysiloxane to blocked isocyanate 15 is between 9:1 and 1:1. The dispersion may also contain minor amounts of other ingredients such as surfactants, pH buffers, etc.

The cured, perfluoroelastomer article may be coated with 20 polysiloxane-blocked isocyanate dispersion by any means commonly employed in the art such as by dipping, spray coating, or by contacting with an applicator. Coating thickness is typically 0.1 to 10 microns, preferably 3 to 7 microns. Generally, the thicker the coating, the less sticky the resulting perfluoroelastomer article. However, as the coating thickness increases, the article's ability to form a good (i.e. non-leaking) seal decreases, so the two properties must be balanced for a particular 25 end use application.

The wet-coated article thus produced is then dried to remove most of the liquid. Drying may be done at any temperature less than the temperature where the blocked isocyanate reacts with the pendant hydroxyl groups on the polysiloxane to form urethane oligomer during the

drying time. Care must be taken not to dry the coating too quickly.

Otherwise, bubbles may form in the coating, which when burst, may result in large non-coated areas on the surface of the article. Typically, drying is done in air at room temperature (20°C).

- 5 The dry-coated article thus produced is then heated to a temperature where the reaction of the blocked isocyanate and pendant hydroxy groups on the polysiloxane occurs during a reasonable period of time, thus forming a cured, durable film of polysiloxane-urethane oligomer on the surface of the perfluoroelastomer article. This will be at a
- 10 temperature greater than 100°C for more than 5 minutes. Often, curing at 200°C for 10 minutes yields an optimum polysiloxane-urethane oligomer film. One skilled in the art will recognize that this period of time will vary depending upon the actual blocked isocyanate and polysiloxane contained in the coating composition. It is not necessary that the resulting film be a
- 15 continuous film of uniform thickness in order for the resulting perfluoroelastomer article to have a greatly improved surface with little or no stickiness. The physical properties of the film-coated articles of this invention have comparable physical properties to non-coated perfluoroelastomer articles.
- 20 To improve the durability (i.e. adhesion) of the film onto the surface of a cured perfluoroelastomer article, the surface of the article may preferably be pre-treated, i.e. prior to application of the dispersion, to increase surface area. Examples of suitable surface treatments for use in this invention include, but are not limited to roll flow, sanding, grinding, and
- 25 plasma or chemical etching. Roll flow refers to a process wherein a cured perfluoroelastomer article and abrasive particles are agitated in a container for a period of time in order to increase the surface area of the article via introduction of microscopic pits, cracks and the like onto the surface. Sanding and plasma or chemical etching increases the article's
- 30 surface area by similar means. Preferably, the surface is also cleaned

with an appropriate solvent to remove contaminants such as mold release agents, lubricants, oils, etc.

The polysiloxane-urethane oligomer film coated perfluoroelastomer articles of this invention are useful in many end use applications such as 5 those involving high temperatures (i.e. 200°C or more) and harsh chemical or plasma environments wherein it is undesirable for the perfluoroelastomer articles to stick to the surfaces of materials with which the articles are in contact. Examples of such end use applications include semiconductor manufacturing equipment and the chemical process 10 industry.

EXAMPLES

TEST METHOD

15 Sticking Force

Stickiness was measured on type AS-214 o-rings. An o-ring was compressed 25% in a jig between two stainless steel plates. The jig was then placed in an air oven for 16 hours at 160°C. Afterwards, the jig was removed from the oven and allowed to cool at room temperature for 3 20 hours. The plates were then attached to an Instron and the force required to pull the plates apart was measured. A sticking force less than 100 N was acceptable, between 100 and 150 N marginal and greater than 150 N unacceptable.

25 Helium Leak Test

A film-coated type AS-214 o-ring was used in a jig to form a seal between a chamber fillable with helium and a chamber under vacuum. The o-ring was compressed 25%. The vacuum chamber was connected to a ULVAC HELIOT 301 Helium Leak Detector. The test was run by 30 measuring the elapsed time between when helium was introduced into the helium chamber and when it was detected at the rate of at least 10^{-10} Pa

m^3/sec by the He detector. An elapsed time of greater than 30 seconds was acceptable, between 30 seconds and 15 seconds marginal, and less than 15 seconds, unacceptable.

5 **Example 1**

The cured perfluoroelastomer articles employed in this Example were type AS-214 o-rings made from a perfluoroelastomer comprising copolymerized units of tetrafluoroethylene, perfluoro(methyl vinyl)ether and perfluoro(8-cyano-5-methyl-3,6-dioxa-1-octene). In addition to 10 perfluoroelastomer, o-rings contained 6.5 phr TiO_2 and 3 phr SiO_2 .
O-rings were spray coated with an ethyl acetate dispersion containing 10 weight percent SAT No. 7 polysiloxane-blocked isocyanate coating composition (available from Shinko Technical Research Company, Ltd.). The coated o-rings were dried in air and then baked in an air oven 15 at 200°C for 10 minutes to yield polysiloxane-urethane oligomer film-coated perfluoroelastomer articles of this invention. The coated o-rings were washed with water. Film thickness was 5 microns.

Sticking force of the film-coated perfluoroelastomer o-rings was measured according to the Test Method. The results for the film coated o-rings of the invention averaged 40 N for 3 o-rings tested. The sticking force of a comparative (i.e. not coated) perfluoroelastomer o-ring was measured as 300 N.

The sealing ability of three other film-coated o-rings prepared above was measured by the He leak test method. The average elapsed time 25 was greater than 60 seconds.

Example 2

The cured perfluoroelastomer articles employed in this Example were type AS-214 o-rings made from a perfluoroelastomer comprising 30 copolymerized units of tetrafluoroethylene, perfluoro(methyl vinyl)ether

and perfluoro(8-cyano-5-methyl-3,6-dioxa-1-octene). In addition to perfluoroelastomer, o-rings contained 6.5 phr TiO₂ and 3 phr SiO₂.

A set of 3 o-rings was spray coated with an ethyl acetate dispersion containing 10 weight percent SAT No. 7; another set of 3 o-rings was 5 spray coated with a 10 wt.% solution of SAT No. 7A; 3 other o-rings with SAT No. 7B; and 3 other o-rings with SAT No. 7C polysiloxane-blocked isocyanate coating composition (available from Shinko Technical Research Company, Ltd.). The various coating solutions (7, 7A, 7B and 7C) differed in the weight ratio of polysiloxane to isocyanate. The coated 10 o-rings were dried in air and then baked in an air oven at 250°C for 15 minutes to yield polysiloxane-urethane oligomer film-coated perfluoroelastomer articles of this invention. Film thickness was 3 microns.

Sticking force of film-coated perfluoroelastomer o-rings was 15 measured according to the Test Method. The results for the film coated o-rings of the invention averaged less than 40 N for each set of 3 o-rings coated with SAT No. 7, 7A, 7B and 7C. The sticking force of a comparative (i.e. not coated) perfluoroelastomer o-ring was measured as 300 N.

20 Four fresh sets of 3 o-rings each were prepared as above, coated with SAT No. 7, 7A, 7B and 7C, respectively. The average sealing ability of each of these sets was measured by the He leak test method. The average elapsed time for each set was greater than 60 seconds.